

Relating Ocean Optics to Photochemical Transformations of Dissolved Organic Carbon in Coastal Waters

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LONG-TERM GOALS

The two long-term goals of this research are (1) to use remotely sensed ocean optical data for estimates of the regional and global scale significance of photochemistry involving colored dissolved organic matter (CDOM) and (2) to produce high quality quantitative data on photochemical fading of CDOM that will allow forward prediction of the effect of this process on inherent optical properties in the sea.

OBJECTIVES

The central objective of this research program is to examine quantitatively the links between optical measurements and photochemical organic carbon transformations in the sea. Our goal is to establish quantitative methods to relate variability in water-leaving radiance to photochemical reactions that lead to direct loss of CDOM and consequent changes in UV optical properties in the photic zone. By examining these quantitative relationships, we also hope to gain both an understanding of the dominant variables controlling UV optics in the mixed layer and the critical parameters influencing DOC photochemical reactions in seawater.

APPROACH

Reaching these objectives requires a wavelength dependent description of the *in situ* optical field for ultraviolet radiation (UV) together with spectral efficiency data for photooxidation of CDOM. Our general approach uses three connected principles:

- (1) Diffuse attenuation coefficients (K_d) of UV radiation can be related to ocean color using ratios of near-surface water-leaving radiance to measured K_d (Johannessen et al., 2001).
- (2) CDOM is the dominant contributor to the absorption and attenuation of UV in coastal waters. Consequently, in most cases, diffuse attenuation of UV can be related directly to absorption by dissolved organic matter (Johannessen et al., 2001).
- (3) The absorption of UV by CDOM leads to photochemical transformations that include the destruction of chromophores and production of lower-molecular weight compounds. Wavelength-dependent apparent quantum yield (AQY) for these transformations can be determined experimentally.

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With measurements of solar radiation and upwelling radiance at the sea-surface, we estimate photochemical transformations of surface-layer DOM by applying empirical relationships between: (1) reflectance and diffuse attenuation, (2) spectral diffuse attenuation and UV absorbance, and (3) UV absorbance and action spectra for photochemical transformations.

Field optical data are collected with two instruments (Satlantic, Inc.) that add UV measurements to visible wavebands compatible with the SeaWiFS ocean color satellite. The first is a modified Tethered Spectral Radiometer Buoy (TSRB-II) which simultaneously measures incident irradiance (E_d) and upwelling radiance (L_u) in 14 wavebands, including 4 in the UV (2 nm bandwidth). The second is a SeaWiFS Profiling Multichannel Radiometer (SPMR) which measures vertical profiles of downwelling irradiance in wavebands identical to the TSRB-II, chlorophyll fluorescence (WETStar miniature flow through fluorometer), conductivity, and temperature. Both instruments are deployed simultaneously to accumulate UV/VIS optical data (E_d , L_u , & K_d) while collecting discrete rosette samples at the same station for evaluation of CDOM absorption.

Laboratory irradiations (on shore and at sea) are used to quantify the efficiency of CDOM photochemistry. Using a 1.5kW Xe lamp, sequential long-pass optical filters, and a statistical evaluation (as described by Rundel, 1983 and Cullen and Neal, 1997) of the resulting photochemical rates, we calculate an AQY spectrum for photochemical and coincident physical/chemical (ex. fading) alterations of the CDOM with a single irradiation. This novel approach is much faster than traditional monochromatic techniques (3 hrs vs. 3 weeks), allowing study of both spatial and temporal variations in AQY spectra, not previously possible with other approaches. By combining AQY data, CDOM absorbance, irradiation profiles, and solar spectral irradiance, we calculate both whole water column and depth discriminated photochemistry. Accurate determination of AQY spectra is critical to our effort.

Using relationships developed by deployments of the TSRB-II and SPMR with discrete measurements of CDOM absorptivity, we then combine ocean colour data with irradiance, mixing and water optical models to estimate the photomineralization of CDOM in the coastal ocean. These data represent the beginning of regional photochemical inventories and a starting point for both long term regional scale studies and short-term prediction of photochemical carbon transformations in the coastal ocean.

At Dalhousie, Lori Ziolkowski (technician), and a graduate student, Cedric Fichot, (M.Sc.), have the ONR project as their primary effort. The PI, W. L. Miller, oversees the effort with daily contact. Optical efforts benefit from the participation of J.J. Cullen's group (w/ R. Davis) also at Dalhousie and assistance from Satlantic, Inc. (instrument development, optical expertise, field and computer assistance). This year, our field collaborations were with Drs. R. Powell (LUMCON) and W. Landing (Florida State University) on two cruises to the Gulf of Mexico. We have continued collaboration with D. Kieber and K. Mopper (NSF funding) along with M. A. Moran and R. Zepp (ONR funding) on data analysis and reporting from fieldwork done during previous reporting periods.

WORK COMPLETED

One ONR sponsored student (Cedric Fichot) began his program to evaluate the use of remote sensing to drive photochemical models in the surface ocean, spending the summer "mining" optical data sets from previous ONR efforts at Dalhousie.

We staged for and participated in two cruises in the Gulf of Mexico, adding significantly to our optical data set relating Lu_{vis} to Kd_{UV} and Kd_{UV} to a_{CDOM} .

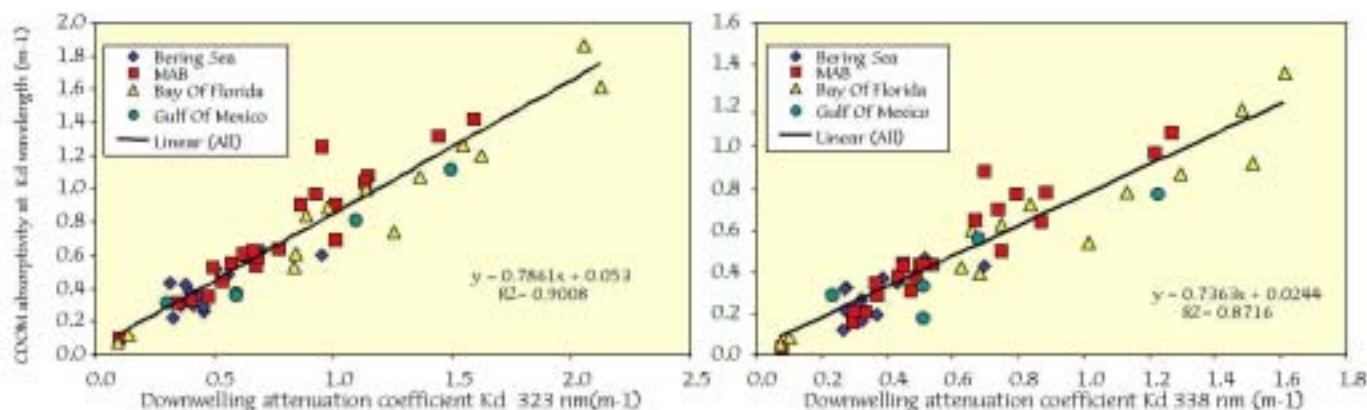
We used our novel multispectral irradiation system to evaluate the spatial and temporal variations in CDOM fading efficiency, a critical component to future models of CDOM transformations.

We submitted two more manuscripts for publication and completed revisions for one other.

We streamlined and modified our MATLAB® code to determine CDOM fading efficiency surfaces (GUI, graphical user interface, etc.) and modified programs to assimilate the results into a mixed layer model that predicts CDOM fading in coastal waters.

RESULTS

New samples and optical data from diverse water types add confidence to our optical relationships that will be used in predicting photochemistry from remotely sensed data. The data set amassed over the last 4 years, produces algorithms (relating Kd at 323, 338, and 380 nm to $Lu_{412/555}$) that allow estimates of *in situ* UV attenuation to be made from remotely sensed ocean color in the visible and to calculate CDOM absorptivity from these Kd 's. This year, we added optical data sets from the Gulf of Mexico (Figure 1).



1. Expanded data set for relating downwelling attenuation to CDOM absorptivity.
[graph: positive linear trends, $R^2 > 0.87$, between CDOM absorptivity (nr^1) & Kd at 323 and 338 nm]

The statistical approach to calculating quantum efficiency surfaces for CDOM fading (250 separate AQY curves) that we described in previous reporting periods provides a rapid and useful tool for quantification of CDOM fading in the mixed layer. It allowed evaluation of temporal and spatial variation in AQY surfaces, an example shown in Figure 2. This result suggests that a single AQY surface for CDOM fading (defined for each wavelength as Δa_{CDOM} / moles photons absorbed) does not apply over the exposure history of the water sample, with maximum AQY increasing by a factor of 10 over 6 days of exposure in our solar simulator (2 days exposure ~ 1 week in the surface ocean).

These two quantitative results allow several oceanic evaluations. First using the optical relationships outlined above, SeaWiFS imagery can be used to calculate inherent CDOM optical properties such as the calculation of the spectral slope coefficient (S) for a_{CDOM} (Figure 3b). This should eventually provide a significant improvement in remote estimates of chlorophyll which currently correct for CDOM interferences with a constant S value. Second, using our quantitative model of CDOM fading kinetics which incorporates three linked modules (radiative transfer, surface layer mixing, and photochemical processes: described in previous report periods) we can evaluate the spectral effect of changing AQY surfaces for CDOM fading on prediction of CDOM absorptivity (Figure 3a). It is clear from this result that the predicted evolution of CDOM optical properties will depend strongly on selection of appropriate AQY surfaces.

IMPACT / APPLICATIONS

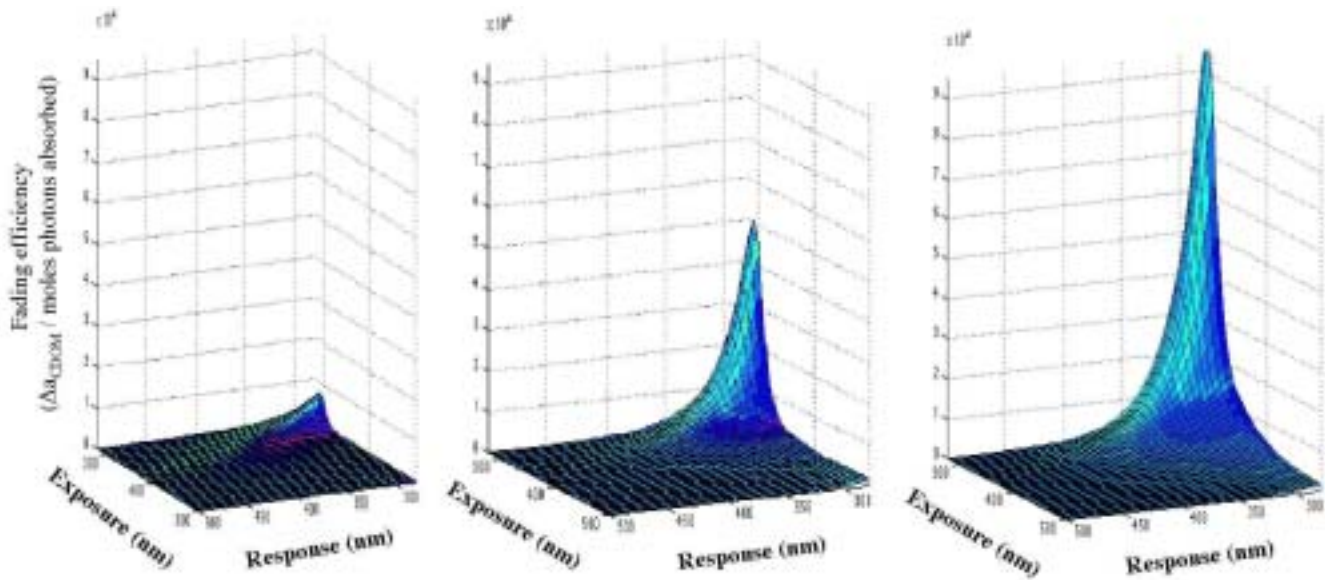
The optical properties of CDOM in the ocean control photochemical rates, effect oceanic chemical cycles, and influence the interpretation of ocean color (Miller, 1998). Our multispectral approach to defining and modeling CDOM fading indicates that variability must be defined in this critical component if predictive capability for CDOM dynamics is going to be addressed. Our novel, multispectral approach to AQY determinations is gaining acceptance and use in the photochemical community and should produce new insights. The links between ocean optics and photochemical carbon transformations will provide a unique ability to address the regional and global significance of photochemical reactions in the ocean. Our approach to estimating variations in the CDOM slope coefficient (S) from remotely sensed visible data may prove a valuable tool in correcting chlorophyll algorithms.

TRANSITIONS

The optical system we have assembled will continue to produce opportunities to expand our optical database through collaborative cruise opportunities. We have advised several researchers on developing similar techniques for optical measurements (Mopper, ODU) and solar simulation (M. Wells, U. Maine; L. Melot, York University). During the reporting period we have exchanged K_d and L_u (305, 323, 338, 380, 412, & 443 nm) and a_{CDOM} spectral data with Neil Blough (1998, Mid Atlantic Bight, University of Maryland), Rodney Powell (2001, Gulf of Mexico, LUMCON), and David Kieber (2000, Gulf of Maine, SUNY, Syracuse). Our MATLAB[®] algorithms and irradiation techniques are shared with groups within Dalhousie. AQY data for CO photochemistry has been shared with O. Zafiriou (2000, Gulf of Maine and BATS, WHOI) and AQY data for production of biological products was exchanged with Mary Ann Moran (2000, Sapelo Island Marsh, University of Georgia) and Richard Zepp (2000, Sapelo Island Marsh, U.S. EPA, Athens, GA).

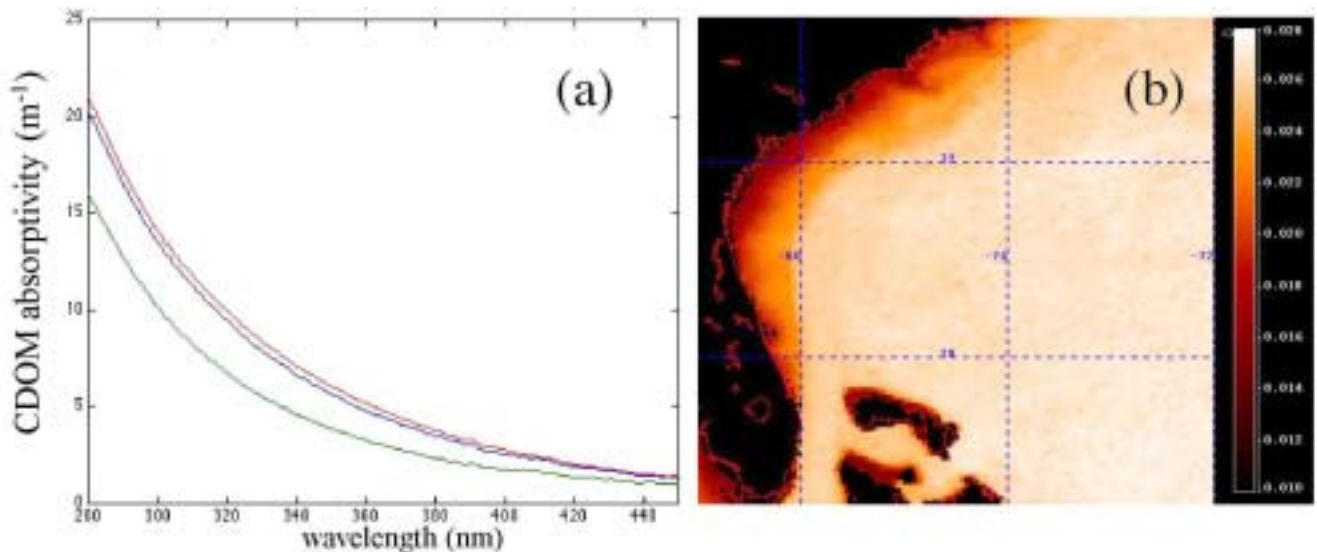
RELATED PROJECTS

In addition to fieldwork, collaborations, and results stated above, my NSERC grants support related photochemical studies (DMS photolysis, etc.), allowing cost effective methods development for both projects. In July 2001, we began work on the NSERC funded Canadian SOLAS Network which will address ocean atmosphere interactions. Cruises are planned for the Pacific and Atlantic and we will make ONR related optical measurements and perform fading experiments on samples collected.



2. The effect of exposure history on photochemical efficiency for CDOM fading in coastal seawater.

[3 dimensional efficiency surfaces (x =exposure wavelength, y =spectral response, z =efficiency of response (/m/moles photons absorbed)) show highest values for fading at UV wavelengths caused by irradiation with UV radiation. Efficiency increases as fading proceeds in time: left = week 1, middle = week 2, right = week 3 (middle = 2 x left, right = 5 x left)]



3. Use of quantitative results for ocean predictions/observations.

[graph (a): modeled a_{CDOM} spectra (6 day, full sun, 5 meter MLD) showing little fading (blue) and greater fading (green) for the smallest and largest AQY surfaces in Fig. 2 respectively]
[graph (b): satellite picture of Georgia Bight in July, 1999 showing higher calculated CDOM slope coefficients (S) near the coast relative to the open ocean]

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